

VERIFICATION OF TRANSLATION

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[Material Name] Specification 1

[Material Name] Abstract 1

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[Document Title] SPECIFICATION

[Title of the Invention] LAMINATE AND PROCESS FOR PRODUCING THE SAME

[Patent claims]

[Claim 1] A laminate, comprising: a polymer substrate comprising a cyclized rubber which is a conjugated diene polymer cyclized product or a derivative thereof, and a thin film laminated on the surface of the polymer substrate by a dry film-forming method.

[Claim 2] The laminate according to claim 1, wherein the derivative of the conjugated diene polymer cyclized product is a compound produced by introducing a polar group into the conjugated diene polymer cyclized product by a modifying reaction using a polar-group-containing compound.

[Claim 3] A process for producing a laminate, comprising the step of laminating a thin film, on a surface of a polymer substrate produced by incorporating a conjugated diene polymer cyclized product or a derivative thereof by a dry film-forming method.

[Detailed Explanation of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a laminate and a process for producing the same, more specifically, a laminate which is good in adhesiveness between its substrate and its thin film laminated thereon by a dry film-forming method such as a chemical vapor growth method or a vacuum evaporation method even if the substrate is a polymer substrate made of a nonpolar polymer; and a process for producing the same.

[0002]

[Prior Art]

Hitherto, metal vapor deposited products, in which metal is vapor-deposited on plastic products, have widely been used as food containers and others since they have good decorative property, gas barrier property and light blocking property, and laminate films each obtained by vapor-depositing a silicon oxide film on a plastic film have been used for wrapping materials and others that have transparency and a high gas barrier property.

However, when they are made using, as a starting material thereof, a nonpolar polymer such as polypropylene resin or polyethylene resin, there arise problems that the adhesiveness between the polymer and a thin film vapor-deposited thereon is poor and the film is easily peeled.

[0003]

In order to solve such problems, there is known a method of subjecting a plastic molded body or plastic film surface to physically surface-roughening treatment by corona discharge,

flame radiation, radioactive ray radiation or the like and using anchor effect based on this treatment to improve the adhesiveness of the roughened surface to a thin film vapor-deposited. There is also known a method of applying a polar polymer such as polyester resin or polyamide resin onto the roughened surface and then vapor-depositing a metal thereon. However, even if such methods are used, the adhesiveness of the vapor-deposited thin film is insufficient.

[0004]

Suggested is also a method of incorporating an additive into a plastic material, thereby improving the adhesiveness of the plastic to the film vapor-deposited thereon. Examples thereof include a method of incorporating, into polypropylene, a maleic anhydride modified polypropylene in which maleic anhydride is graft-polymerized (Patent Document 1), and a method of incorporating magnesium oxide and magnesium silicate into a crystalline propylene- α -olefin copolymer (Patent Document 2).

[0005]

[Patent Document 1] Japanese Patent Application Laid-Open (JP-A) No. 50-61469

[Patent Document 2] JP-A No. 8-104977

[0006]

[Problems to be solved by the Invention]

In light of the above-mentioned situations, the present invention has been made, and an object thereof is to provide a laminate which is good in adhesiveness between its substrate and its thin film laminated thereon by a dry film-forming method such as a chemical vapor growth method or a vacuum evaporation

method even if the substrate is a polymer substrate made of a nonpolar polymer, and a process for producing the same.

[0007]

[Means for solving the problem]

The inventors have repeated eager researches to solve the above-mentioned problems, so as to find out that the adhesiveness between a polymer substrate and a thin film thereon by a dry film-forming method can be remarkably improved by incorporating a cyclized rubber in the polymer substrate. Based on this finding, the present invention has been accomplished.

[0008]

Accordingly, according to the present invention, the following invention aspects 1 to 3 are provided:

1. A laminate comprising: a polymer substrate comprising a cyclized rubber which is a conjugated diene polymer cyclized product or a derivative thereof and a thin film laminated on the surface of the polymer substrate by a dry film-forming method.
2. The laminate in which the derivative of the conjugated diene polymer cyclized product is a compound produced by introducing a polar group into the conjugated diene polymer cyclized product by a modifying reaction using a polar-group-containing compound.
3. A process for producing a laminate, comprising the step of laminating a thin film, on a surface of a polymer substrate produced by incorporating a conjugated diene polymer cyclized product or a derivative thereof into a polymer-molding material, by a dry film-forming method.

[0009]

[Modes for Carrying Out the Invention]

Hereinafter, the present invention will be explained in detail.

The laminate of the present invention is characterized by comprising: a polymer substrate comprising a cyclized rubber which is a conjugated diene polymer cyclized product or a derivative thereof, and a thin film laminated on the surface of the polymer substrate by a dry film-forming method.

[0010]

The cyclization ratio of the cyclized rubber used in the present invention is usually 10% or more, preferably from 40 to 95%, more preferably from 60 to 90%. When the cyclization ratio is within this range, the property for improving the adhesiveness of the thin film becomes good.

The cyclization ratio is the following value: at each of times before and after cyclization reaction of the conjugated diene polymer, the peak area of protons originating from the double bonds therein is measured by proton NMR analysis; the percentage of the double bonds remaining in the cyclized product is obtained by regarding the area before the cyclization reaction as 100; and a value represented by the calculation equation = (100 - the percentage of the double bonds remaining in the cyclized product) is calculated.

[0011]

The weight-average molecular weight of the cyclized rubber is a value measured by GPC (the value being a value in terms of standard polystyrene), and is usually from 1,000 to 1,000,000, preferably from 10,000 to 500,000, more preferably

from 30,000 to 300,000. If the weight-average molecular weight (Mw) of the cyclized rubber is too small, the adhesiveness of the thin film tends to lower. Conversely, if the weight-average molecular weight (Mw) is too large, a primer layer having a uniform film thickness tends not to be easily formed.

[0012]

The glass transition temperature (Tg) of the cyclized rubber is not particularly limited, and can be appropriately selected in accordance with the use purpose. The Tg is usually from -50 to 200°C, preferably from 0 to 100°C, more preferably from 20 to 90°C, in particular preferably from 30 to 70°C. If the Tg of the cyclized rubber is over these ranges, a problem about the handle-ability thereof may be caused.

[0013]

The cyclization degree (n) of the cyclized rubber, that is, the linking of the rings is usually in the range of 1 to 3. The amount of gel in the cyclized rubber is usually 10% or less by weight, preferably 5% or less by weight. It is particularly preferred that the cyclized rubber is a cyclized rubber which does not substantially have any gel. If the gel amount is large, the surface smoothness of the polymer substrate comprising the cyclized rubber may lower, or the adhesiveness of the thin film may deteriorate.

[0014]

The conjugated diene polymer cyclized product is a product obtained by (co)polymerizing a conjugated diene monomer, or a conjugated diene monomer and another monomer copolymerizable with the conjugated diene monomer to produce a conjugated diene polymer, and then cyclizing the polymer in the presence of an

acid catalyst.

[0015]

Examples of the conjugated diene monomer include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 2-phenyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, and 3-butyl-1,3-octadiene. These monomers may be used alone or in combination of two or more thereof.

[0016]

Examples of the monomer copolymerizable with the conjugated diene monomer include aromatic vinyl monomers such as styrene, o-methylstyrene, p-methylstyrene, m-methylstyrene, 2,4-dimethylstyrene, ethylstyrene, p-tert-butylstyrene, α -methylstyrene, α -methyl-p-methylstyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, p-bromostyrene, 2-methyl-1,4-dichlorostyrene, 2,4-dibromostyrene, and vinyl naphthalene; linear olefin monomers such as ethylene, propylene and 1-butene; cyclic olefin monomers such as cyclopentene and 2-norbornene; non-conjugated diene monomers such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene; (meth)acrylic acid esters such as methyl (meth)acrylate, and ethyl (meth)acrylate; (meth)acrylonitrile; and (meth)acrylamide. These may be used alone or in combination of two or more thereof.

[0017]

The content of the conjugated diene monomer units in the conjugated diene polymer is appropriately selected as long as

the advantageous effects of the present invention are not damaged, and is usually 40% or more by mole, preferably 60% or more by mole, more preferably 80% or more by mole. If this content is small, the cyclization ratio is not easily made high. Thus, the expected effect of improving the physical properties tends not to be easily obtained.

[0018]

It is advisable that the polymerizing method for the conjugated diene polymer is in accordance with a usual method. For example, the polymerization is conducted by solution polymerization or emulsion polymerization using a catalyst known in the prior art, such as a Ziegler polymerization catalyst containing titanium or the like as a catalyst component, an alkyl lithium polymerization catalyst, or a radical polymerization catalyst.

[0019]

Specific examples of the conjugated diene polymer include natural rubber (NR), styrene-butadiene rubber (SBR), polyisoprene rubber (IR), polybutadiene rubber (BR), isoprene-isobutylene copolymerized rubber (IIR), ethylene-propylene-diene copolymerized rubber, and butadiene-isoprene copolymerized rubber (BIR). Of these, polyisoprene rubber (IR) and polybutadiene rubber (BR) are preferred.

[0020]

Usually, the cyclization of the conjugated diene polymer is conducted by dissolving the conjugated diene polymer into a hydrocarbon solvent and then causing the polymer to react in the presence of an acid catalyst.

The acid catalyst may be an acid catalyst that is ordinarily used for cyclization reaction, and examples thereof include sulfuric acid; organic sulfonic acid compounds, such as organic sulfonic acids such as fluoromethanesulfonic acid, difluoromethanesulfonic acid, p-toluenesulfonic acid, anhydrides thereof, and alkyl esters thereof; and metal halides such as trifluoroboron, trichloroboron, tetrachlorotin, tetrachlorotitanium, aluminum chloride, diethylaluminum monochloride, ethylammonium chloride, aluminum bromide, antimony pentachloride, tungsten hexachloride, and iron chloride. These acid catalysts may be used alone or in combination of two or more thereof. Of these, organic sulfonic acid compounds are preferred, and p-toluenesulfonic acid is more preferred.

[0021]

The used amount of the acid catalyst is usually from 0.05 to 10 parts by weight, preferably from 0.1 to 5 parts by weight, more preferably from 0.3 to 2 parts by weight for 100 parts by weight of the conjugated diene polymer.

[0022]

The hydrocarbon solvent used in the reaction is not limited to any especial kind if the solvent does not hinder the cyclization reaction. Examples thereof include aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene; aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, and n-octane; and alicyclic hydrocarbons such as cyclopentane and cyclohexane. Of these, solvents having a boiling point of 70°C or higher are preferred. The solvent used in the polymerization reaction for the conjugated

diene polymer can be used as it is. In this case, the acid catalyst is added to the polymerization reaction solution in which the polymerization has been ended.

The used amount of the solvent is in such a range that the concentration of solid contents of the conjugated diene polymer is usually from 5 to 60% by weight, preferably from 20 to 40% by weight.

[0023]

The cyclization reaction can be conducted under any one of applied pressure, reduced pressure, and atmospheric pressure. The reaction is desirably conducted under atmospheric pressure from the viewpoint of easiness of operation therefor. When the reaction is conducted in dry gas flow, in particular in the atmosphere of dry nitrogen or dry argon, side reactions originating from water content can be restrained.

It is advisable to decide the reaction temperature or the reaction time in accordance with a usual method. The reaction temperature is usually from 50 to 150°C, preferably from 80 to 110°C, and the reaction time is usually from 0.5 to 10 hours, preferably from 2 to 5 hours.

[0024]

Usually, the thus-obtained conjugated diene polymer cyclized product is obtained as a solid by inactivating the cyclizing catalyst, removing the residue of the cyclizing catalyst and removing the inactive solvent in a usual way.

[0025]

It is possible to use, as the derivative of the conjugated diene polymer cyclized product, a compound produced by introducing a polar group into the conjugated diene polymer

cyclized product by a modifying reaction using a polar-group-containing compound.

[0026]

The polar-group-containing compound, which is used in the modifying reaction, is not limited to any especial kind if the compound is a compound capable of introducing a polar group into the conjugated diene polymer cyclized product. Examples thereof include ethylenic unsaturated compounds having a polar group such as an acid anhydride, carboxyl, hydroxyl, thiol, ester, epoxy, amino, amide, cyano or silyl group, or a halogen.

The polar group is preferably an acid anhydride, carboxyl, hydroxyl, ester, epoxy or amino group, and is more preferably an acid anhydride, carboxyl or hydroxyl group since the group is good in effect of improving the adhesiveness of the thin film.

[0027]

Examples of the compound having an acid anhydride or carboxyl group include maleic anhydride, itaconic anhydride, aconitic anhydride, norbornenedicarboxylic anhydride, acrylic acid, methacrylic acid, and maleic acid. Of these, maleic anhydride is preferably used from the viewpoint of reactivity and economy.

[0028]

Examples of the compound containing a hydroxyl group include hydroxyalkyl esters of an unsaturated acid, such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; unsaturated acid amides having a hydroxyl group, such as N-methylol(meth)acrylamide, and N-(2-hydroxyethyl)(meth)acrylamide; polyalkylene glycol monoesters of an unsaturated acid, such as polyethylene glycol

mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, and poly(ethylene glycol-propylene glycol) mono(meth)acrylate; and polyhydric alcohol monoesters of an unsaturated acid such as glycerol mono(meth)acrylate. Of these, hydroxyalkyl esters of an unsaturated acid are preferred, and 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate are more preferred.

[0029]

Examples of the ethylenic unsaturated compound having some other polar group include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, glycidyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, (meth)acrylamide, and (meth)acrylonitrile.

[0030]

The method for introducing the polar-group-containing compound into the conjugated diene polymer cyclized product is not particularly limited. In the case of adding an ethylenic unsaturated compound thereto, it is in general advisable to conduct the introduction in accordance with a known reaction called ene-addition reaction or graft polymerization reaction.

This addition reaction is conducted by causing the conjugated diene polymer cyclized product to react with the polar-group-containing compound optionally in the presence of a radical generator. Examples of the radical generator include peroxides such as di-tert-butylperoxide, dicumylperoxide, benzoylperoxide, tert-butylperoxide benzoate, methyl ethyl ketone peroxide; and azonitriles such as dimethyl 2,2'-azobis(2-methylpropionate).

[0031]

The addition reaction may be conducted in a solid phase state or in a solution state. The reaction is preferably conducted in a solution state since the reaction is easily controlled. Examples of the used solvent are the same as the above-mentioned hydrocarbon solvents in the cyclization reaction.

[0032]

The used amount of the polar-group-containing compound is appropriately selected, and is in such a range that the rate of the introduced polar group is usually from 0.1 to 200 millimoles, preferably from 1 to 100 millimoles, more preferably from 5 to 50 millimoles per 100 g of the modified cyclized rubber.

[0033]

The reaction for introducing the polar group can be conducted under any one of applied pressure, reduced pressure, and atmospheric pressure. The reaction is desirably conducted under atmospheric pressure from the viewpoint of easiness of operation therefor. When the reaction is conducted in dry gas flow, in particular in the atmosphere of dry nitrogen or dry argon, side reactions originating from water content can be restrained.

It is advisable to decide the reaction temperature or the reaction time in accordance with a usual method. The reaction temperature is usually from 30 to 250°C, preferably from 60 to 200°C, and the reaction time is usually from 0.5 to 5 hours, preferably from 1 to 3 hours.

[0034]

If necessary, the cyclized rubber may further contain additives such as a filler, an antistatic agent, an age resistor,

a lubricant, a crosslinking agent, an anti-blocking agent, a colorant, a light ray blocking agent, and an ultraviolet absorbent.

[0035]

The polymer substrate used in the present invention is a substrate in which the above-mentioned cyclized rubber is incorporated into a polymer-molding material. The incorporated amount of the cyclized rubber is usually from 0.1 to 50 parts by weight, preferably from 0.5 to 20 parts by weight, more preferably from 1 to 10 parts by weight for 100 parts by weight of the polymer-molding material. If the incorporated amount is too small, the adhesiveness of the thin film thereto tends to be poor. Conversely, if the amount is too large, mechanical strength of the polymer substrate may lower.

[0036]

Examples of the polymer-molding material which constitutes the polymer substrate in the present invention include thermoplastic resin, curing resin, and elastomer.

[0037]

Examples of the thermoplastic resin include hydrocarbon resin, polyester resin, polyamide resin, polyimide resin, polyetherimide resin, polysulfone resin, polyethersulfone resin, polyetheretherketone resin, polycarbonate resin, polyvinyl butyrate resin, and polyarylate resin.

[0038]

Examples of the curing resin include acrylic resin, phenol resin, cresol resin, urea resin, melamine resin, alkyd resin, furan resin, unsaturated polyester resin, epoxy resin, and urethane resin.

In connection with the manner of the curing, for example, the following materials can be listed up: a material cured by irradiation with active radiating rays such as ultraviolet rays or an electron beam; a material cured by polymerizing a monomer with applied heat in the presence of a catalyst; and a material cured by mixing two liquids and then heating the liquids.

[0039]

Examples of the elastomer include vulcanized rubbers such as natural rubber, polybutadiene rubber, styrene-butadiene rubber, and acrylonitrile-butadiene rubber; olefin thermoplastic elastomers, styrene thermoplastic elastomers, polyester thermoplastic elastomers, and polyamide thermoplastic elastomers.

[0040]

The polymer substrate made of any non-polar polymer out of the above-mentioned polymers causes the adhesiveness thereof to the thin film to be remarkably improved. Examples of such a non-polar polymer include hydrocarbon resins. Of these, linear olefin resin and cyclic olefin resin are preferred.

[0041]

Specific examples of the linear olefin resin include homopolymers and copolymers made from an α -olefin having 2 to 4 carbon atoms, such as ethylene, propylene or butene. Of these, polyethylene and polypropylene resins are preferred and polypropylene resin is more preferred from the viewpoint of multiusability.

[0042]

The polypropylene resin is not limited to any especial kind if the resin is a polymer or copolymer obtained by

polymerizing monomers made mainly of propylene. Examples thereof include a homopolymer from propylene, propylene-ethylene random copolymer, propylene- α -olefin random copolymer, and propylene-ethylene- α -olefin ternary polymers.

[0043]

An example of the cyclic olefin resin is norbornene-based resin described in JP-A No. 7-231928. Such a norbornene-based resin is a resin obtained by polymerizing materials containing at least a norbornene-based monomer. Examples thereof include (i) a ring-opened (co)polymer of a norbornene-based monomer, and polymers subjected to polymer-modification such as addition of maleic acid or addition of cyclopentadiene as the need arises; (ii) resin in which the (i) is hydrogenated; (iii) resin obtained by addition-polymerizing a norbornene-based monomer; and (iv) resin obtained by addition-copolymerizing a norbornene-based monomer with an olefin monomer such as ethylene or an α -olefin. The method for the polymerization and the method for the hydrogenation can be conducted in a usual way.

[0044]

Examples of the norbornene-based monomer include norbornene and alkyl- and/or alkylidene-substituted products such as 5-methyl-2-norbornene, 5-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene and 5-ethylidene-2-norbornene, and polar-group-substituted products thereof, which are substituted with a polar group such as a halogen; dicyclopentadiene and 2,3-dihydrodicyclopentadiene; dimethanooctahydronaphthalene, alkyl- and/or alkylidene-substituted products thereof, and

polar-group-substituted products thereof, which are substituted with a polar group such as a halogen, for example, 6-methyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-ethyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-ethylidene-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-chloro-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-cyano-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, 6-pyridyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene, and 6-methoxycarbonyl-1,4:5,8-dimethano-1,4,4a,5,6,7,8,8a-octahydronaphthalene; an adduct of cyclopentadiene and tetrahydroindene or the like; trimers or tetramers of cyclopentadinene, for example, 4,9:5,8-dimethano-3a,4,4a,5,8,8a,9,9a-octahydro-1H-benzoindene, and 4,11:5,10:6,9-trimethano-3a,4,4a,5,5a,6,9,9a,10,10a,11,11a-dodecahydro-1H-cyclopentaanthracene.

[0045]

The norbornene-based resin which can be used in the present invention is preferably a resin in which the weight-average molecular weight, which is measured by gel permeation chromatography (GPC) using a toluene or cyclohexane solvent, is usually from 1,000 to 1,000,000, preferably from 10,000 to 500,000, more preferably from 20,000 to 100,000. If

the weight-average molecular weight is too small, the physical strength of the polymer substrate may be poor. Conversely, if it is too large, the resin may not be molded with ease.

[0046]

When the norbornene-based resin is a resin obtained by hydrogenating a ring-opened polymer made from a norbornene-based monomer, the hydrogenation ratio thereof is preferably 90% or more, more preferably 95% or more, in particular preferably 99% or more from the viewpoint of resistance against thermal deterioration, resistance against optical deterioration and others.

[0047]

The polymer may be used alone or in combination of two or more thereof.

[0048]

If necessary, the polymer-molding material may contain, besides the above-mentioned polymer, additives such as a filler, an antistatic agent, an age resistor, a lubricant, a crosslinking agent, an anti-blocking agent, a colorant, a light ray blocking agent, and an ultraviolet absorbent.

[0049]

The method for incorporating the cyclized rubber into the polymer-molding material is not particularly limited. Usually, a method of melting and kneading the components is adopted.

[0050]

The shape of the polymer substrate is not particularly limited, and examples thereof are various shapes dependently on a final product, such as spherical, rodlike, columnar, plate, sheet, and film forms.

[0051]

The polymer substrate is usually molded by a molding method known in the prior art, and then used. Examples of the molding method include extrusion molding, cast molding, calendar molding, vacuum molding, injection molding, inflation molding, and blow molding.

[0052]

Examples of the molded product of the polymer substrate include a film molded product, an injection molded product, an extrusion molded product, a vacuum molded product, and a blow molded product. Of these, a film molded product and an injection molded product can be preferably used.

[0053]

The film molded product may be, for example, a non-oriented film molded by extrusion molding or cast molding, or may be a oriented film produced by drawing this non-oriented film by a drawing method such as monoaxial drawing, tenter-system sequential biaxial drawing, tenter-system simultaneous biaxial drawing, or tubular system simultaneous biaxial drawing. Of these, an oriented film can be preferably used.

The thickness of the film is appropriately selected in the accordance with the use purpose thereof, and is usually from 1 to 1,000 μm , preferably from 5 to 500 μm , more preferably from 10 to 200 μm .

The width or the length of the film is not particularly limited, and is appropriately selected in the accordance with the use purpose.

[0054]

The thin film in the present invention is a film laminated on the surface of the polymer substrate by a dry film-forming method.

[0055]

In the present invention, the dry film-forming method is usually a method of converting a metal, a metal oxide, an organic material or the like into gas, and then forming the film on a surface of a substrate. This method is classified into a physical film-forming method and a chemical film-forming method.

[0056]

Examples of the physical film-forming method include vacuum vapor-deposition, sputtering, ion plating, and ion implantation.

Examples of the chemical film-forming method include chemical vapor depositions (CVDs) such as thermal CVD, optical CVD, plasma enhanced CVDs (such as microwave CVD and high frequency CVD).

[0057]

Examples of the material of the thin film include metals such as aluminum, zinc, nickel, zirconium, gold, silver, tin, indium, titanium and chromium; metal oxides such as silicon oxide, aluminum oxide, magnesium oxide, and zirconium oxide; metal nitrides such as SiN, CrN, TiN and TiAlN; and materials a typical composition of which is C_xH_y .

[0058]

The film thickness of the thin film is not particularly limited, and is usually from 1 nm to 100 μm , preferably from 10 nm to 10 μm .

[0059]

The selection of the material of the thin film makes it possible to yield a laminate having the following functions: for example, colorability, masking property, lubricity, anti-blocking property, antistatic property, gas barrier property, water vapor barrier property, water resistance, hydrophilicity, abrasion resistance, defogging property, easy-writable property, and lusterless property.

[0060]

The thin film may be formed on the whole surface of the polymer substrate, may be partially formed, or may be formed into a specific pattern.

[0061]

The laminate of the present invention may be a product produced by forming, on the surface of the above-mentioned thin film, a mono-layered or multi-layered film made of materials different from the material of the thin film by a dry film-forming method.

[0062]

The process for producing a laminate of the present invention is characterized in that the step of laminating a thin film, on a surface of a polymer substrate produced by incorporating a conjugated diene polymer cyclized product or a derivative thereof by a dry film-forming method.

[0063]

It is advisable that conditions for the dry film-forming method are appropriately selected in accordance with the kind of the adopted dry film-forming method, the material of the thin film, and the film thickness of the thin film.

[0064]

The laminate of the present invention can be used for various purposes, and can be preferably used as, for example, automobile exterior members such as a bumper, a corner bumper, a bumper air-dam skirt, a mud guard, a side braid, a wheel cap, a spoiler, a side step, and a door mirror base; automobile interior members such as an instrument panel, a lever, a knob, a dashboard, and a door liner; electrical equipment parts such as a connector, a cap plug, a pot, a refrigerator, lighting equipment, audio equipment, and OA equipment; daily necessities such as a color box and a storage case; and gas barrier wrapping films such as food wrappings for cup noodles, confectionery, vegetables, and so on, and textile wrappings for shirts, T-shirts, panty hose, and so on. The film vapor-deposited with a metal can be in particular preferably used for wrappings for foods, such as potato chips, for which moisture-proofing and oxygen barrier property are necessary.

[0065]

[Examples]

The present invention will be more specifically described by the following examples. The word "part(s)" and the symbol "%" in the following description are those based on weight unless otherwise specified.

[0066]

Analysis and evaluation were made as follows:

(1) Weight-average molecular weight (Mw) of each polymer

The weight-average molecular weight (Mw) was obtained as a value in terms of standard polystyrene by gel permeation chromatography.

(2) Cyclization ratio of each cyclized rubber

The cyclization ratio was obtained by $^1\text{H-NMR}$ analysis in accordance with a method described in the following documents (i) and (ii).

(i) M. a. Golub and J. Heller. Can. J. Chem, 41, 937 (1963), and

(ii) Y. Tanaka and H. Sato, J. Polym. Sci: Poly. Chem. Ed., 17, 3027 (1979).

[0067]

(3) Amount of polar groups in each modified cyclized rubber

A cyclized rubber modified with maleic anhydride has an acid anhydride group originating from the added maleic acid and a carboxyl group obtained by the hydrolysis of the acid anhydride group. The Fourier transform infrared spectrum of this cyclized rubber was measured, and the strength of the peak (1760 to 1780 cm^{-1}) of the acid anhydride group was measured, and then the content of the acid anhydride group was obtained by a calibration curve method. In the same way, the strength of the peak (1700 cm^{-1}) of the carboxyl group was measured, and then the content of the carboxyl group was obtained by a calibration curve method.

The hydroxyl value of each cyclized rubber modified with a hydroxyl-containing compound was measured according to a method described in "Standard Oil and Fat Analysis Test method (Japan Oil Chemists' Society)" 2, 4, 9, 2-83. From this hydroxyl value, the amount of hydroxyl in the modified cyclized rubber was calculated.

[0068]

(4) Adhesiveness (observation with a transmission electron

microscope)

A cross section of each obtained laminate film was observed with a transmission electron microscope, and the adhesiveness of its silicon oxide film was judged on the following criterion. The results are shown in Table 1.

O: The silicon oxide was not peeled over the whole of the observed cross section.

X: The silicon oxide was peeled over the whole of the observed cross section.

[0069]

(Synthesis Example 1)

Into a pressure resistant reactor equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen gas introducing tube were charged 300 parts of polyisoprene (cis-1,4 units: 73%, trans-1,4 units: 22%, 3,4-units: 5%, weight-average molecular weight: 174,000) cut into pieces 10 mm cubic together with 700 parts of toluene (polymer concentration: 30%). The reactor was purged with nitrogen, and then heated to 80°C. While the solution was stirred, the polyisoprene was completely dissolved into toluene. Thereafter, 2.07 parts of p-toluenesulfonic acid (anhydrous) was charged into the solution to conduct cyclization reaction at 80°C. After about 4 hours, a 25% solution of sodium carbonate in water, containing 0.8 part of sodium carbonate, was charged into the solution to quench the reaction. The solution was stirred at 80°C for 30 minutes. Thereafter, 2 parts of a filtration aid (Radio Light) was added thereto, and a filter (GA-100, manufactured by Advantec Toyo Kaisha, Ltd.), made of glass fiber and having pores of 1 μ m diameter, was used to remove the residue of the catalyst.

To this solution was added 0.3 part of an age resistor (Irganox 1010, manufactured by Chiba Specialty Chemicals), and then toluene was removed at 160°C. When the concentration of solid contents in the solution turned into 70 to 75% by weight, the solution was poured into a metal vat coated with a fluorine-contained resin, and then dried under a reduced pressure at 75°C so as to yield a cyclized rubber A. The resultant cyclized rubber A was analyzed. The results are shown in Table 1.

[0070]

(Synthesis Example 2)

A cyclized rubber B was yielded in the same way as in Synthesis Example 1 except that polyisoprene containing 68% of cis-1,4 units, 25% of trans-1,4 units and 7% of 3,4-units and having a weight-average molecular weight of 92,100 was used as polyisoprene, the used amount of p-toluenesulfonic acid (subjected to reflux and dehydration so as to set the amount of water content to 150 ppm or less in toluene) was changed to 2.81 parts, and the reaction was quenched by charging a 25% solution of sodium carbonate in water, containing 1.08 parts of sodium carbonate. The resultant cyclized rubber B was analyzed. The results are shown in Table 1.

[0071]

(Synthesis Example 3)

Into a pressure resistant reactor equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen gas introducing tube were charged 300 parts of polyisoprene (cis-1,4 units: 70%, trans-1,4 units: 24%, 3,4-units: 6%, weight-average molecular weight: 141,000) cut into pieces 10 mm cubic together with 700

parts of toluene (polymer concentration: 30%). The reactor was purged with nitrogen, and then heated to 80°C. While the solution was stirred, the polyisoprene was completely dissolved into toluene. Thereafter, 2.69 parts of p-toluenesulfonic acid (anhydrous) were charged into the solution to conduct cyclization reaction at 80°C. After about 4 hours, a 25% solution of sodium carbonate in water, containing 1.03 parts of sodium carbonate, was charged into the solution to quench the reaction. The solution was stirred at 80°C for 30 minutes. Thereafter, 2 parts of a filtration aid (Radio Light) were added thereto, and a filter (GA-100, manufactured by Advantec Toyo Kaisha, Ltd.), made of glass fiber and having pores of 1 μ m diameter, was used to remove the residue of the catalyst.

To this solution was added 0.3 part of an age resistor (Irganox 1010, manufactured by Chiba Specialty Chemicals), and then toluene was removed at 160°C. When the concentration of solid contents in the solution turned into 70 to 75% by weight, 9 parts of maleic anhydride were charged into the solution to conduct reaction at 180°C for 1 hour. After the reaction, unreacted maleic anhydride and toluene were removed while nitrogen was caused to flow at 180°C. Thereafter, the resultant was dried under a reduced pressure at 75°C so as to yield a modified cyclized rubber C. The resultant modified cyclized rubber C was analyzed. The results are shown in Table 1.

[0072]

(Synthesis Example 4)

Into a pressure resistant reactor equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen gas introducing tube were charged 300 parts of polyisoprene (cis-1,4 units: 68%,

trans-1,4 units: 25%, 3,4-units: 7%, weight-average molecular weight: 92,100) cut into pieces 10 mm cubic together with 700 parts of toluene (polymer concentration: 30%). The reactor was purged with nitrogen, and then heated to 80°C. While the solution was stirred, the polyisoprene was completely dissolved into toluene. Thereafter, 2.07 parts of p-toluenesulfonic acid (anhydrous) were charged into the solution to conduct cyclization reaction at 80°C. After about 4 hours, a 25% solution of sodium carbonate in water, containing 0.8 part of sodium carbonate, was charged into the solution to quench the reaction. The solution was stirred at 80°C for 30 minutes. Thereafter, 2 parts of a filtration aid (Radio Light) were added thereto, and a filter (GA-100, manufactured by Advantec Toyo Kaisha, Ltd.), made of glass fiber and having pores of 1 μ m diameter, was used to remove the residue of the catalyst.

To this solution was added 0.3 part of an age resistor (Irganox 1010, manufactured by Chiba Specialty Chemicals), and then toluene was removed at 160°C. When the concentration of solid contents in the solution turned into 50 to 60% by weight, 15 parts of hydroxyethyl acrylate and 1.5 parts of an azo type initiator, ACHN (1,1-azobis-1-cyclohexanecarbonitrile), were charged into the solution to conduct reaction at 140°C for 1 hour. After the reaction, unreacted hydroxyethyl methacrylate and toluene were removed while nitrogen was caused to flow at 140°C. Thereafter, the solution was poured into a metal vat coated with a fluorine-contained resin, and then dried under a reduced pressure at 75°C so as to yield a modified cyclized rubber D. This cyclized rubber D was analyzed. The results are shown in Table 1.

[0073]

(Example 1)

Five parts of the cyclized rubber A, 95 parts of polypropylene (F-200S, manufactured by Idemitsu Kosan Co., Ltd.) and 0.01 part of Irganox 1010 (manufactured by Chiba Specialty Chemicals) were mixed in a Henschel mixer, and then a biaxial extruder was used to melt and knead the mixture at 200°C to yield pellets. A monoaxial extruder was used to extrude the pellets from a multi-manifold shaped T die at a resin temperature of 250°C and a cooling roll temperature of 30°C, thereby yielding a sheet of 1000 μm thickness. This sheet was drawn 5 times in the lengthwise direction with a drawing roll heated to 125°C, and next the sheet was drawn 10 times in the lateral direction in a tenter in which hot wind of 155°C temperature was circulated. Furthermore, the sheet was thermally set at 70°C for 2 seconds to yield a biaxial-oriented film. The thickness of the film was 25 μm .

[0074]

A winding type vacuum evaporation device was used, SiO₂ (manufactured by SUMITOMO TITANIUM CORPORATION) was used as a vapor-deposited material, and this was vaporized onto a face of the resultant film in a high-frequency heating manner. Under a condition that the pressure was 8×10^{-5} Torr, a silicon oxide film of 25 nm thickness was laminated onto the face.

[0075]

The adhesiveness of the silicon oxide film in the resultant laminate film was evaluated by observation with a transmission electron microscope. The result is shown in Table 1.

[0076]

(Examples 2 to 4)

The same way as in Example 1 was performed except that the cyclized rubber A was changed into each of the (modified) cyclized rubbers B to D, so as to yield laminates in which a silicon oxide film was laminated. The adhesiveness of the silicon oxide film in each of the films was evaluated by observation with a transmission electron microscope. The results are shown in Table 1.

[0077]

(Comparative Example 1)

A laminate film in which a silicon oxide film was laminated was yielded in the same way as in Example 1 except that the cyclized rubber A was not incorporated and the amount of the incorporated polypropylene (F-200S, manufactured by Idemitsu Kosan Co., Ltd.) was changed into 100 parts. The adhesiveness of the silicon oxide film in this film was evaluated by observation with a transmission electron microscope. The result is shown in Table 1.

[0078]

Table 1

	Examples				Comparative Example
	1	2	3	4	1
(Modified) cyclized rubber	A	B	C	D	-
Weight-average molecular weight	134,800	73,000	113,800	76,000	-
Cyclization ratio	74	75	79	75	-
Amount of polar group contained (mmol/100g)	-	-	23	-	-
Anhydride group	-	-	25	-	-
Carboxyl group	-	-	-	36	-
Hydroxyl group	-	-	-	-	-
Adhesiveness of the thin film	○	○	○	○	x

[0079]

It is understood from Table 1 that the oriented film of polypropylene into which no cyclized rubber was incorporated was a laminate very poor in adhesiveness to the silicon oxide thin film (Comparative Example 1) while the oriented films of polypropylene in which the cyclized rubber of the present invention was incorporated were good in adhesiveness to the silicon oxide thin film (Examples 1 to 4).

[0080]

[Effect of the Invention]

According to the present invention, provided are a laminate which is good in adhesiveness between its substrate and its thin film laminated thereon by a dry film-forming method such as a chemical vapor growth method or a vacuum evaporation method even if the substrate is a polymer substrate made of a nonpolar polymer, and a process for producing the same. This laminate can be applied to various usages.

[Document Title]

ABSTRACT

[Abstract]

[Object] The present invention provides a laminate which is good in adhesiveness between its substrate and its thin film laminated thereon by a dry film-forming method such as a chemical vapor growth method or a vacuum evaporation method even if the substrate is a polymer substrate made of a nonpolar polymer, and a process for producing the same.

[Means of solution] A laminate, comprising: a polymer substrate comprising a cyclized rubber which is a conjugated diene polymer cyclized product or a derivative thereof, and a thin film laminated on the surface of the polymer substrate by a dry film-forming method.

[Selected Drawings] None